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COARSENING KINETICS OF Fe_3C PARTICLES IN Fe – 0.67 %C STEEL

KINETYKA KOAGULACJI CEMENTYTU W STALI Fe – 0.67 %C

Kinetics of Fe_3C particle coarsening in Fe-0.67%C steel for of two materials (A, B) of different microstructures (with different matrix (ferrite) grain size and particles distribution) was investigated. In material A, obtained by quench-hardening with subsequent tempering, the particles are mainly at grain (subgrain) boundaries of fine-grained matrix formed by in situ recrystallization of ferrite. In material B, obtained by recrystallization after cold rolling (10%), particles are mainly inside grains of coarse-grained matrix – formed by discontinuous recrystallization of ferrite.

During annealing (at 680, 700 i 715°C up to 800 hours) the microstructure morphology of A and B is preserved; the material microstructure determines the particle coarsening rate, it is lower in B. Analysis of empirical kinetic functions with the LSW theory suggest that higher particle coarsening rate in A results from higher diffusivity of Fe along the matrix grain boundaries. Lower particle coarsening rate in B results from matrix diffusion of C and Fe.

Keywords: disperse phase, Ostwald ripening, particle coarsening

Przedmiotem pracy jest kinetyka koagulacji cząstek cementytu w stali Fe-0.67% C, w postaci dwóch materiałów (A, B) różniących się mikrostrukturą (wielkością ziarna osnowy (ferryt) i rozmieszczeniem cząstek). W materiale A, otrzymanym w wyniku wysokiego odpuszczania zahartowanej stali, większość cząstek jest na granicach ziarn drobnoziarnistej, zrekrystalizowanej in situ, osnowy. W materiale B, otrzymanym podczas wyżarzania rekrystalizującego stali materiału A, po odkształceniu plastycznym na zimno (10%), cząstki są przeważnie wewnątrz ziarn gruboziarnistej, zrekrystalizowanej w sposób nieciągły, osnowy.

Podczas wyżarzania izotermicznego (przy temperaturach 680, 700 i 715°C i czasach do 800 godz.) stwierdzono zachowanie morfologii mikrostruktury (w A i B) oraz większą szybkość koagulacji w materiale A. Interpretacja empirycznych równań kinetycznych za pomocą teorii koagulacji LSW sugeruje, że przyczyną większej szybkości koagulacji cząstek w materiale A jest dominująca rola dyfuzji węgla i żelaza na granicach ziarn osnowy. Natomiast wolniejsza koagulacja w materiale B jest związana z objętościową dyfuzją składników stali w osnowie.

1. Introduction

Most of experimental studies of Ostwald ripening were carried out on disperse carbide phases in steels, in particular, cementite (Fe_3C). They show that matrix microstructure (ferrite) is essential for cementite coarsening. There is a lot of experimental data for coarsening kinetics of cementite particles situated at matrix grain boundaries [1]. Their interpretation is significantly reduced by limited data for coarsening of particles situated primarily inside matrix grains. It could result from difficulties in carrying out controlled recrystallization of plastically deformed ferrite, in the presence of cementite particles of the coarse spheroidite (higher content

of cementite at low dispersion) giving the required microstructure of the steel.

The aim of the present work was investigation of cementite coarsening for two different microstructures of coarse spheroidite in a medium carbon steel. In the first case particles were situated mainly at matrix grain boundaries, in the other case particles were situated mainly in matrix grains [2, 3]. For discussion of the results, the Lifshitz-Slezow-Wagner theory (LSW) [1] was applied.

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2. Experimental

2.1. Materials and heat treatment

For investigation a non-alloy Fe-0.67% C steel was used. The steel composition is given in Table 1. 100 mm long pieces from rectangular rod (8×12mm

cross-section) were homogenized for 10 hours at 1200°C in argon atmosphere. A coarse spheroidite was produced by:

- austenitizing at 900°C for 2 hours,
- quenching into 5% caustic soda solution;
- tempering at 700°C for 150 hours in vacuum (10^{-2} Tr).

TABLE 1

Chemical composition of Fe-0.67%C steel									
Element content [wt.%]	C	Mn	Si	P	S	Cr	Ni	Cu	Fe
	0.67	0.27	0.20	0.011	0.016	0.07	0.04	0.07	Balance

A part of the material was cold rolled with $\epsilon = 10\%$ deformation. Then, the both materials (deformed and non-deformed) were annealed at 700°C for 5 hours in vacuum. The so annealed material was the starting material for investigation of cementite coarsening. Material which was only annealed was marked by A and material which was deformed and annealed was marked by B.

From both materials A and B specimens (5.5×8×10 mm) were taken for cementite coarsening. The specimens were annealed at 680°C, 700°C and 715°C up to 800 hours in vacuum ($\sim 10^{-2}$ Tr). For given coarsening conditions (temperature and time) specimens from the both materials (A, B) were annealed together. Cementite coarsening was analysed metallographically by light microscopy.

2.2. Qualitative metallography

Planar surface of specimens was polished mechanically and double etched: (i) in nital (for revealing ferrite grain boundaries); (ii) in boiling alkaline sodium picrate (for colouring Fe₃C particles – to distinguish them from ferrite grains).

The microstructure of A material in the initial state (0 h) and after the longest annealing time (800 h at 700°C) is shown in Figure 1. In the initial state (Fig. 1a), most particles are at grain boundaries of in situ recrystallized fine-grained matrix. The particles are generally at the junction of three grains, what determines their shape. The shape of individual particle sections are mainly convex, however there occur also some non-convex particle agglomerations in which the convex parts could be well recognized. During annealing particle growth (coarsening) and matrix grain growth take place. One can see that during annealing, the microstructure morphology is in principle preserved.

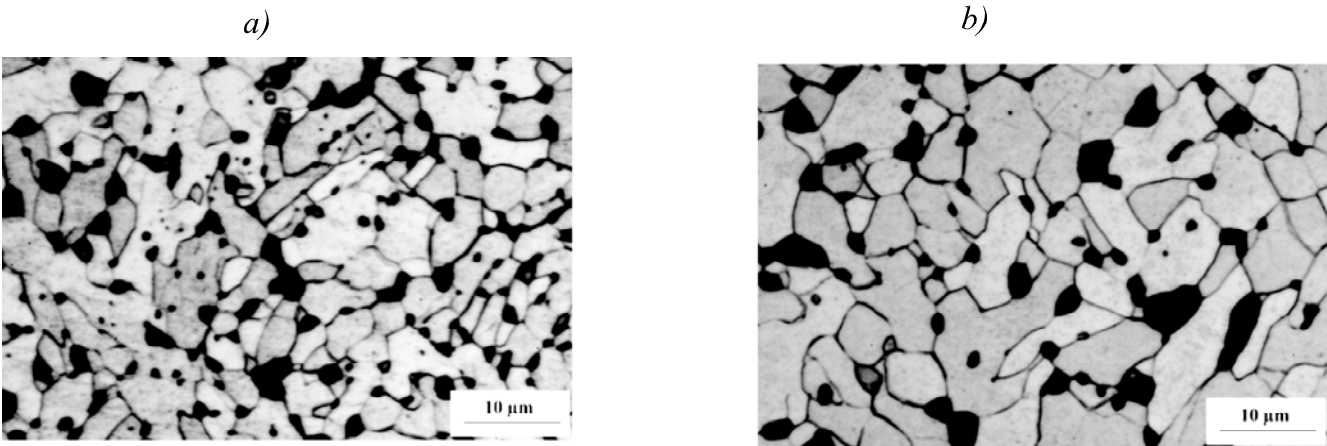


Fig. 1. Microstructures of Fe-0.67%C steel (material A) during cementite particle coarsening at 700°C: a) $t=0$ h, b) $t=800$ h

The microstructure of material B in the initial state and after the longest annealing time (800 h at 700°C) is shown in Figure 2. In the initial state (Fig. 2a), most particles are in grains of discontinuous recrystallized coarse-grained matrix. Particles inside grains are mainly of a circular shape. Particles at grain boundaries are slightly larger; isolated particles are convex. The ma-

trix grain boundaries are curved. Particles at boundaries of two grains indicate the so-called Zener drag effect. During annealing particle growth (coarsening) take place which is less pronounced than in case of material A. The matrix grain size is slightly changed. The microstructure morphology is preserved, Figure 2b.

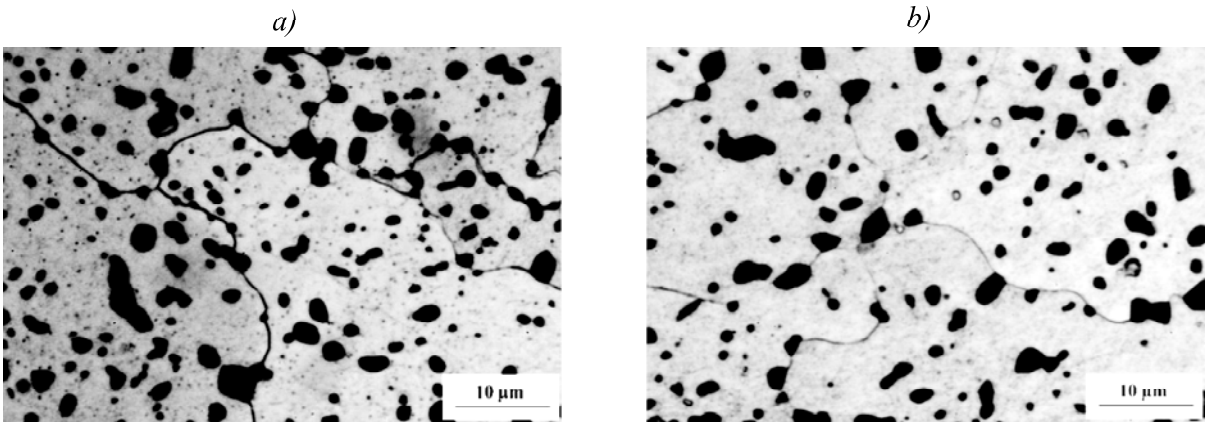


Fig. 2. Microstructures of Fe-0.67%C steel (material B) during cementite particle coarsening at 700°C: a) $t=0$ h, b) $t=800$ h

2.3. Quantitative metallography

For quantitative description of cementite particles the specific mean curvature of its surface (M_V) was used. The M_V parameter may be easily measured by stereological method, based on Bodziony equation [4]:

$$M_V = 2\pi N_A, \tag{1}$$

where N_A is the density of particle profiles on a planar section of the material [5]. According to Eq. (1) the estimation of M_V parameter may be reduced to the N_A parameter measurement by counting of profiles in test quadrates, positioned disjointly and randomly on microstructure images. The N_A parameter measurements were carried out on 24 microstructure images for material A and on 40 pictures for B (for each annealing time), measurement area was a quadrate with real surface area $A = 1,37 \cdot 10^{-3} \text{ mm}^2$.

3. Coarsening kinetics of cementite particles

3.1. Empirical kinetic equations

In isothermal conditions of particle coarsening, M_V is a function of time t , $M_V(t)$. Empirical function $M_V(t)$

was determined for the three coarsening temperatures (680, 700 and 715°C). Values of the $M_V(t)$ for different annealing times (t) are given in Table 2, while Figures 3 and 4 present graphs of the functions.

TABLE 2

Empirical kinetic $M_V(t)$ functions

$t, \text{ h}$	$M_V \cdot 10^{-5}, \text{ mm}^{-2}$					
	A	B	A	B	A	B
	680°C		700°C		715°C	
0	5.78	5.76	5.86	5.83	4.86	5.59
50	—	—	4.94	5.70	—	—
100	—	—	4.67	5.55	—	—
150	5.12	5.51	—	—	3.76	5.28
200	—	—	4.16	5.29	—	—
300	4.37	5.24	—	—	3.15	4.93
400	—	—	3.49	4.65	—	—
600	3.55	4.74	—	—	2.35	4.35
800	—	—	2.64	4.28	—	—

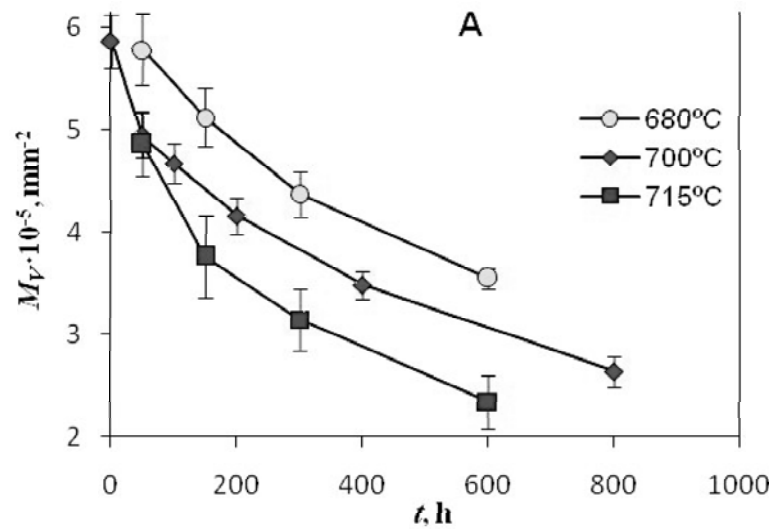


Fig. 3. Empirical kinetic $M_V(t)$ functions, (material A)

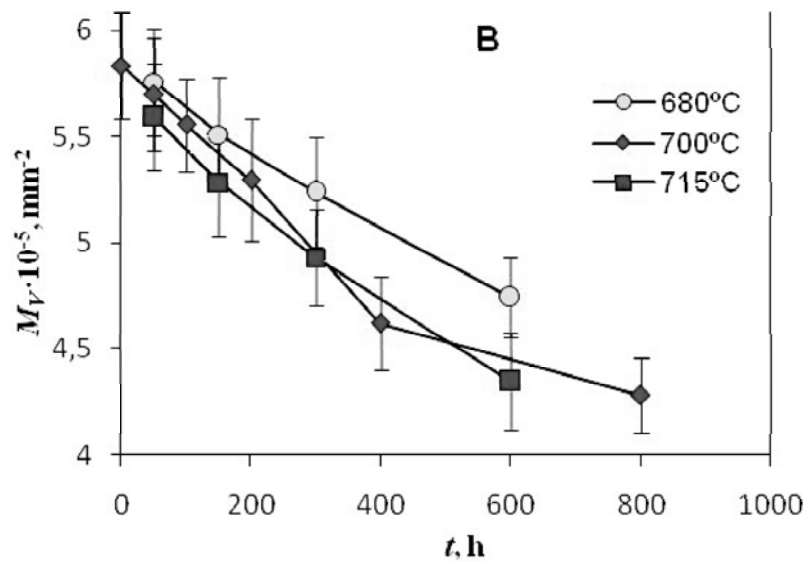


Fig. 4. Empirical kinetic $M_V(t)$ functions, (material B)

The $M_V(t)$ functions are decreasing. At 700°C annealing temperature, the $M_V^{(t)}$ function values for B are larger and the decreasing rate is significantly smaller than for A (Fig. 5). This means that for B, the coarsening of cementite particles is slower. Table 2 shows that for 800 hour coarsening at 700°C, the relative change of

$M_V(t)$ is: for material B, 27%, and for A, 55%. For B, the average cementite coarsening rate is approximately twice smaller than for A. This conclusion is confirmed by empirical $M_V(t)$ functions for temperatures 680 and 715°C (Table 2).

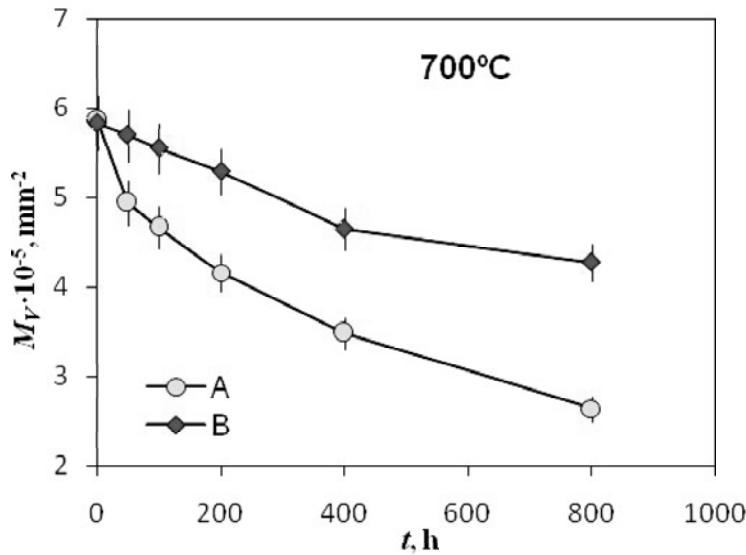


Fig. 5. Empirical kinetic $M_V^{(t)}$ functions, (700°C)

Figure 3 shows the empirical $M_V(t)$ functions for material A at different temperatures. Though the temperatures used were relatively close each other, the graphs differ significantly (for different functions the areas of variation do not overlap). They confirm, what was expected, that cementite coarsening rate is an increasing function of temperature. By contrast, in Figure 4 (material B; empirical $M_V(t)$ function at different temperatures) the differences between various functions are not clear. In particular, for the time $t = 400$ hours some irregularity occurs i.e., the $M_V(t)$ for 700°C is lower than the estimated value for 71°C.

Some further analysis of the empirical $M_V(t)$ functions in terms of the LSW@ theory can provide additional information about the effect of temperature on coarsening kinetics of cementite particles.

3.2. Theoretical description of empirical $M_V(t)$ functions

To describe the coarsening kinetics of cementite, the LSW kinetic equation was used in the form

$$M_V^{-m/2}(t) = M_V^{-m/2}(0)(1 + k_m t), \quad (2)$$

where: m is the parameter which depends on the coarsen-

ing rate controlling mechanism [1], K_m is the coarsening rate constant.

If empirical $M_V(t)$ function is consistent with the LSW theory, there exists a m parameter for which the empirical $M_V^{-m/2}(t)$ function is linear. Graphs of the empirical function $M_V^{-m/2}(t)$ for materials A and B indicate approximate linearity for different m (2, 3 and 4) [3]. Because of this ambiguity it is difficult to specify the m parameter (analogous situation is in [6, 7 and 8]). Consequently, to evaluate the parameter m statistical regression analysis was used. Average m for different coarsening temperatures (680, 700 and 715°C) is, for A, $m = 3.6$, and for B, $m = 3.2$. Figures 6 and 7 present the empirical $M_V^{-m/2}(t)$ functions and their linear approximation, respectively, for material A and B. The empirical functions are linear (only for B at 700°C and $t = 400$ hrs., the $M_V^{-m/2}(t)$ -value is clearly beyond the regression line, Fig 4 and 7). According to the LSW theory, in the first approximation one can assume that for A, $m = 4$, the coarsening kinetics of cementite is determined by diffusion processes in the matrix, dominated by grain boundary diffusion. In contrast, for B, $m = 3$, the coarsening kinetics is determined by matrix volume diffusion. This interpretation is consistent with the microstructure of the A and B materials (Fig. 1 and 2), and with results of other works [1] as well.

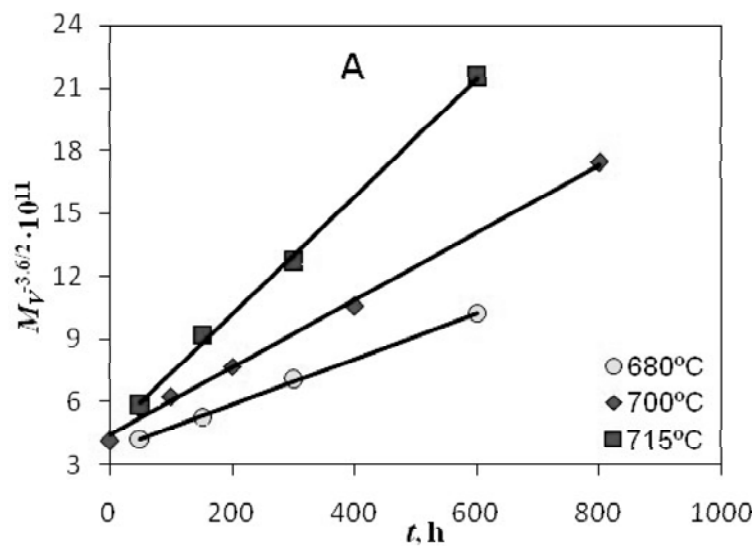


Fig. 6. Empirical kinetic $M_V^{-3.6/2}(t)$ functions, (material A)

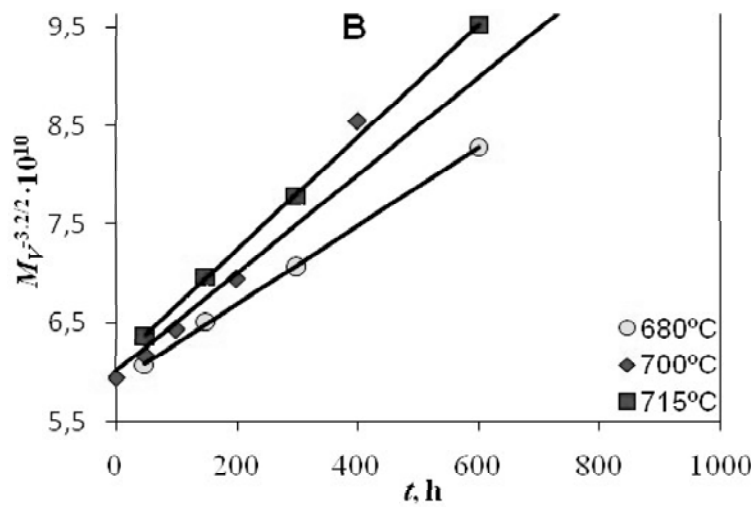


Fig. 7. Empirical kinetic $M_V^{-3.2/2}(t)$ functions, (material B)

Figures 6 and 7 show the regression lines $M_V^{-m/2}(t)$ for $m = 3.6$ and $m = 3.2$, respectively. The regression coefficients (which are directly proportional to the value of coarsening rate constants K_m (for $m = 3.6$ and $m = 3.2$), are the increasing functions of temperature. For materials B, the temperature dependence of the empirical rate constant K_m is clearly weaker than for A.

3.3. Empirical activation energy of coarsening and diffusion coefficient

On the basis of the LSW theory, it is possible to evaluate the temperature effect on cementite coarsening. For determination of the empirical activation energy of cementite coarsening the following formula can be used [1, 9]

$$K_m T = a \exp\left(-\frac{Q}{RT}\right), \tag{3}$$

where Q is the empirical activation energy of coarsening, and a is a constant.

Figure 8 shows that the empirical relation $\ln(K_m T) \sim 1/T$ for materials A and B are approximately linear, and therefore are consistent with (3). Empirical activation energy, Q , is: for A, $Q = 215.6$ kJ/mol, while for B, $Q = 88.3$ kJ/mol. For B, due to the small range of K_m temperature variation and scatter of the empirical $M_V(t)$ function values (Table 2 and Fig. 3 and 4), the empirical activation energy $Q = 88.3$ kJ/mol is biased with a large random error.

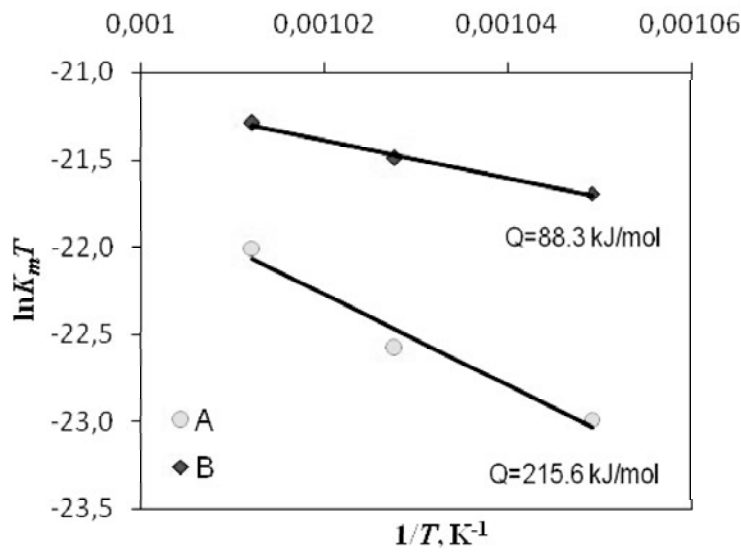


Fig. 8. Empirical relation $\ln(K_m T) \sim 1/T$ for A and B materials

The obtained results indicate that: (i) in material A the coarsening occurs rapidly, with higher activation energy Q , the grain boundary diffusion is dominant ($m \approx 4$); (ii) in B the coarsening occurs slowly, with lower activation energy, the volume diffusion is dominating ($m \approx 3$).

An analysis of diffusion in the matrix can provide information about cementite coarsening rate for materials A and B. As already mentioned, different m values ($m = 2, 3, 4$) can be assigned to empirical $M_V(t)$ functions. Approximately, $m \approx 3$ can be assumed for A and B. The volume diffusion coefficient ($m \approx 3$), during coarsening is given by the formula [1]

$$D = \frac{9RTK}{8\sigma c_\infty V_m^2}, \tag{4}$$

where: c_∞ is the equilibrium solubility of carbon in ferrite, σ is the surface free energy of cementite (J/m^2), R is the gas constant $R = 8.314 \text{ (J/K mol)}$, T is the temperature (K), V_m is the molar volume of cementite. For materials A and B (at $T = 715^\circ\text{C}$) the empirical K_3 and D values are given in Table 3 (for: $\sigma = 0.7 \text{ J/m}^2$, $c_\infty = 1.27 \cdot 10^{-4} \text{ mol/cm}^3$, $V_m = 26.4 \text{ cm}^3/\text{mol}$ [6, 8]).

TABLE 3
Coarsening rate constant (K_3) and diffusion coefficient (D) (temp. 715°C)

Material	$K_3 \cdot 10^{18}, \text{ cm}^3/\text{s}$	$D \cdot 10^8, \text{ cm}^2/\text{s}$
A	17.10	3.23
B	3.68	0.70

The D value for material B is similar to that obtained by Giddings and co-authors [8] ($D = 3.3 \cdot 10^{-9} \text{ cm}^2/\text{s}$). Giddings at al. assume that D is the coefficient of coupled diffusion of Fe and C in the matrix. If we

assume that for material A, D is the average diffusion coefficient (for volume and grain boundary diffusion), its higher value (compared to the D value for material B) is due to the contribution of grain boundary diffusion. The D value for material A is similar to that obtained by Vedula and Heckel ($D = 6 \cdot 10^{-8} \text{ cm}^2/\text{s}$) [6].

4. Discussion

During annealing of Fe-0.67%C steel with coarse spheroidite microstructure (in A and B materials) the cementite coarsening is uniform (microstructure morphology is preserved). The coarsening is accompanied by changing of particles geometric characteristics (M_V parameter).

For material A, the cementite coarsening rate is approximately twice higher than for B. In the first approximation, coarsening kinetics is consistent with the LSW theory, $m = 4$ (for A) and $m = 3$ (for B).

Empirical activation energy, Q , characterizes the temperature dependence of coarsening rate. For material A, $Q = 216 \text{ kJ/mol}$ – which is comparable with of results other author’s [6, 10], while for B, $Q = 88.3 \text{ kJ/mol}$ is close to that obtained by Dirnfeld and Levin [11] for cementite coarsening after the pearlite spheroidization.

The higher coarsening rate, kinetic parameter $m = 4$ and empirical activation energy $Q = 216 \text{ kJ/mol}$ indicate that the coarsening kinetics of cementite for material A is controlled by the rate of grain boundary diffusion, indicating the diffusion of iron the lower coarsening rate, kinetic parameter $m = 3$ and empirical activation energy $Q = 88 \text{ kJ/mol}$ indicate that the coarsening kinetics of cementite for material B is controlled by the rate of volume diffusion, indicating the coupled diffusion of carbon and

iron in the matrix. Low Q means that the coarsening rate for B (measured by K_3) is a slightly increasing function of temperature (Fig. 7).

5. Conclusions

1. Cementite coarsening kinetics is consistent with the LSW theory.
2. When cementite particles are situated mainly at the matrix grain boundaries, the cementite coarsening kinetics is controlled by grain boundary diffusion ($m = 4$), a relatively high coarsening rate (K_4) is an increasing function of temperature.
3. When cementite particles are situated mainly inside matrix grains, the cementite coarsening kinetics is controlled by coupled volume diffusion of carbon and iron ($m = 3$), a relatively low coarsening rate (K_3) is a slightly increasing function of temperature.

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